Research article

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Ethyl carbamate kinetics in double distillation of sugar cane spirit. Part 2: influence of type of pot still

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This study aimed to assess the influence of the pot still configuration on the reduction of ethyl carbamate content in double-distilled sugar cane spirit, as well as to describe the effects of double distillation on this reduction. Ethyl carbamate is a potentially carcinogenic compound that may be present in high concentrations in sugar cane spirit, and therefore could become a public health problem, as well as a factor hindering Brazilian exports of this beverage. In sugar cane spirit production in Brazil, neither pot still configuration nor distillate reflux and cooling/condensation systems are standardized. In this study, ethanol, copper and ethyl carbamate contents were assessed (GC-MS) in sugar cane spirits that were double-distilled in pot stills with different reflux and cooling systems. Double distillation removed 94–98.5% of ethyl carbamate from sugar cane spirit. Pot stills with high reflux rates (equipped with dephlegmator or rectifying system) were more effective in reducing the ethyl carbamate content in double-distilled sugar cane spirit. Copyright © 2013 The Institute of Brewing & Distilling

Keywords: sugar cane spirit; double distillation; pot still; ethyl carbamate

Introduction

Sugar cane spirit is an alcoholic beverage produced by the distillation of fermented sugar cane juice. Cachaça is the typical and exclusive denomination of Brazilian sugar cane spirit, with an alcohol concentration ranging from 38 to 48% ABV *(1)*. It is the fourth most consumed distilled beverage worldwide and production reaches approximately 1.5 billion litres a year *(2)*.

A great challenge in this sector is the standardization of the beverage along the production chain: sugar cane production, must and starter ferment preparation, fermentation conditions and distillation equipment (pot stills or columns). Although aging this beverage in wooden barrels is an optional step of the production chain, it gives a special taste and quality to the final product.

Ethyl carbamate, also known as urethane ($C_2H_5COONH_2$), can be found in several types of fermented foods and beverages *(3)*. Owing to its carcinogenic potential, the presence of this compound in foods and beverages is important because of the toxicological aspects *(4)*. In several countries, such as Canada, the USA, France, Germany and Switzerland, specific laws are already applied to control the presence of ethyl carbamate in alcoholic drinks *(5)*.

Brazilian law established an upper limit of 150 $\mu g\,L^{-1}$ ethyl carbamate in sugar cane spirits *(6)*, which came into force in July 2012 *(7)*. Concentrations of this contaminant above the aforementioned limit constitute a public health problem, hindering exports of this beverage.

Among the several pathways of formation of ethyl carbamate in beverages, the following are worth mentioning: the presence of urethane precursors, such as urea, citrulline and *N*-carbamyl phosphates; yeast strains and by-products of their metabolism; fermentation parameters, such as temperature, alcohol concentration, acidity, pH and distillation system; light and time of storage after distillation *(8,9)*. Nevertheless, the cyanide ion, formed by the enzymatic degradation of cyanogenic glycosides present in the raw material, is considered the main precursor of ethyl carbamate in distilled beverages. Ethyl carbamate is formed in the process of oxidation of cyanide to cyanate, which reacts with ethanol *(10)*. Although the cyanogenic glycosides present in sugar cane remain unknown, this is a cyanogenic plant *(11)*.

In distilled alcoholic beverages, the reaction to form ethyl carbamate is catalysed by the presence of copper in distillation equipment *(8,10)* as well as by the distillation temperature, increasing the content in the final product *(12)*.

Many cachaças and sugar cane spirits produced in Brazil present higher ethyl carbamate content than the upper permitted limit of 150 $\mu g\,L^{-1}$ *(13–17)*. Since the boiling point of ethyl carbamate is 182–185°C, a well conducted distillation process can monitor the content of this compound in distilled beverages.

Double distillation can reduce the content of ethyl carbamate in distilled beverages. In whisky, for instance, it was observed that only 1% of the ethyl carbamate formed during the first distillation was distilled during the second distillation *(8)*. The 'tail' distillate fraction accumulated 15% of the ethyl carbamate formed and the stillage retained 84% of the ethyl carbamate present in the second distillation.

In sugar cane spirit, double distillation decreased ethyl carbamate content by 97% *(18)*. A mean concentration of 317 $\mu g\,L^{-1}$ ethyl carbamate was detected in 13 samples of commercial cachaça, and the samples presenting the lowest content of this compound (38–48 $\mu g\,L^{-1}$) were double distilled *(19)*. Also,

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redistillation reduced the ethyl carbamate content by up to 92.5% in 15 samples of commercial cachaça *(20)*.

Some authors, who emphasize the importance of the reflux rate in the formation of ethyl carbamate in distilled beverages, observed that cachaças with low contents of ethyl carbamate were obtained using pot stills with high reflux rates *(14,16,17)*.

Studies on the formation of ethyl carbamate during the production process of cachaça, including the fermentation and distillation steps, are essential to develop techniques that enable the production of beverages with a lower content of this contaminant. Therefore, this study aimed to assess the influence of pot still configuration on the reduction of ethyl carbamate content in double-distilled sugar cane spirit, as well as to describe the effects of double distillation on this reduction.

Materials and methods

Commercial sugar cane spirit (41% ethanol v/v), donated by Destilaria Capuava (Piracicaba, SP, Brazil), was diluted with treated water to 28% ABV and redistilled in different gas-heated 37 L copper pot stills (Fig. 1), under the same operational conditions. During this distillation, the ‘head’ (1.1% of the boiler useful volume), ‘heart’ (distillate fraction recovered after the ‘head’ fraction and until the distillate fraction in the condenser outlet presented 60% ABV) and ‘tail’ (distillate fraction recovered after the ‘heart’ fraction and until the distillate fraction in the condenser outlet presented 3% ABV) distillate fractions were separated. The ‘heart’ distillate fraction characterized the double-distilled sugar cane spirit.

The distillate fractions were analysed to quantify ethanol, copper and ethyl carbamate. Ethanol and copper analyses were performed according to Official Brazilian Methods *(6)*.

The analysis of ethyl carbamate was carried out 72 h after sample distillation, since this compound is formed up to 24–48 h after distillation *(8,21)*. The samples were analysed with no previous treatment, in a gas chromatograph (GC) coupled to a mass spectrometer (MS), model GCMS-QP2010 Plus (Shimadzu, Kyoto, Japan), using electron impact ionization with an energy of 70 eV and a chromatography capillary column with polar phase (esterified polyethylene glycol – HP-FFAP; 50 m × 0.20 mm 0.33 μm stationary phase film thickness). The temperatures of the injector and the detector interface were 230 and 220°C, respectively. The following temperature programme was used in the oven: starting with 90°C for 1 min, increasing to 150°C at a rate of 10°C min^{-1}, followed by heating up to 230°C at a rate of 30°C min^{-1}, and remaining at this temperature for 2 min. A volume of 1.0 μL was injected using the splitless injection mode, in duplicate. The carrier gas was helium at a flow rate of 1.2 mL min^{-1}. Selected ion monitoring (SIM) acquisition was employed, monitoring the m/z 62 ions for ethyl carbamate and m/z 75 ions for methyl carbamate, used as the internal standard *(22,23)*. Quantification was performed through comparison of the chromatography results of the samples with an analytical curve obtained using an ethyl carbamate stock solution ($y = 1.90823x - 0.01972$; y = concentration, x = peak area; correlation coefficient = 0.9995), employing 150 μg L^{-1} methyl carbamate as the internal standard.

All the reagents were analytical grade. Ethyl carbamate (99%) and methyl carbamate (98%) were purchased from Sigma-Aldrich (St Louis, MO, USA). For the dilutions, ethanol gradient grade for gas chromatography (Merck, Darmstadt, Germany), and ultrapure water (Milli-Q) were used.

The analytical results obtained for double-distilled sugar cane spirit were analysed using one-way analysis of variance (ANOVA) and the Tukey test ($p < 0.05$), in a randomized block design, with three repetitions per block *(24)*.

Results and discussion

Ethyl carbamate content in the commercial sugar cane spirit analysed was 187.27 μg L^{-1}, whereas in the sugar cane spirits obtained after redistillation the content was as follows: (a) 14.10 μg L^{-1} in

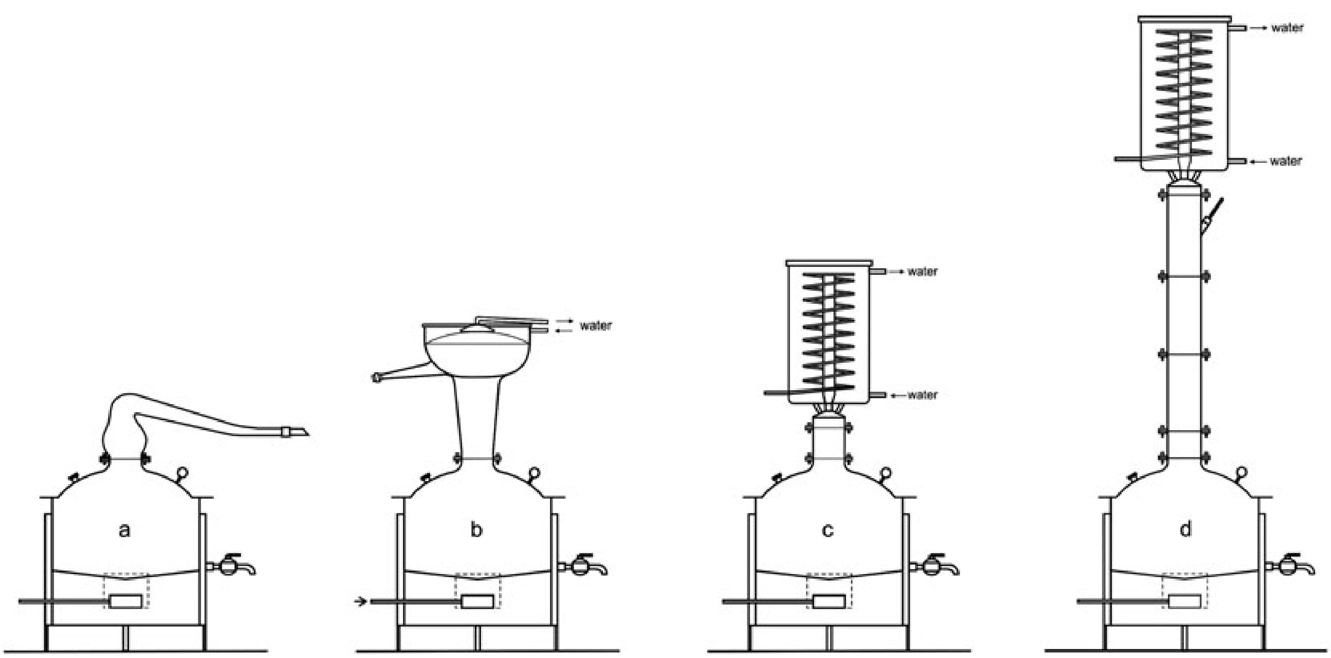

Figure 1. Layout of pot stills used in redistillation to produce double distilled sugar cane spirit: (a) hot head; (b) head cooler; (c) dephlegmator; and (d) rectifier.

hot head pot still; (b) 8.02 μg L^{-1} in head cooler pot still; (c) 7.01 μg L^{-1} in dephlegmator pot still; and (d) 4.42 μg L^{-1} in rectifier pot still. Therefore, the sugar cane spirits obtained after redistillation of the commercial product retained only 5.9, 2.9, 2.7 and 1.5% of the total content of ethyl carbamate formed during the second distillation in hot head, head cooler, dephlegmator and rectifier pot stills, respectively (Table 1).

Similar decreases in ethyl carbamate content were obtained in whisky using double distillation *(8)*. This contaminant was concentrated in the 'tail' distillate fraction as well as in the stillage of the second distillation. The authors reported that, when the ethyl carbamate is formed during the first distillation, it cannot be distilled posteriorly, because the alcohol concentration of the distillate fraction is relatively high. Only a small part (1–2%) of the ethyl carbamate formed in the first distillation remains in the whisky produced. They also reported that the 'tail' distillate fraction of the second distillation presented 15% of the contaminant. The remaining 83–84% of the ethyl carbamate formed in the first distillation was still present in the stillage of the second distillation.

Redistillation reduced the original content of ethyl carbamate by 66.0% to 92.5% in 15 samples of commercial sugar cane spirit *(15)*. The final content of ethyl carbamate in the redistilled beverage was not influenced by the initial alcoholic concentration of the sugar cane spirit *(20)*. In a study carried out to assess ethyl carbamate kinetics in double distillation of sugar cane spirit in a hot head pot still, only 3% of this contaminant remained in the beverage after the second distillation *(18)*.

An average content of 160 μg L^{-1} ethyl carbamate was found in 34 samples of cachaça collected from 28 producers in the state of Rio de Janeiro, Brazil *(14)*. The sample obtained by double distillation in a copper pot still presented 17 μg L^{-1} ethyl carbamate, similar to the sample distilled in a stainless steel pot still, which presented 11 μg L^{-1}.

In our study, the beverages obtained after redistillation of the commercial sugar cane spirit presented the following ethanol concentrations (v/v): (a) 71.2% in the hot head pot still; (b) 72.3% in the head cooler pot still; (c) 76.5% in the dephlegmator pot still; and (d) 79.9% in the rectifier pot still. Since all of the pot stills were under the same operational conditions, taking into consideration the alcohol concentration of the sugar cane spirits obtained after redistillation, it was possible to affirm that the products from the dephlegmator and rectifier pot stills underwent higher reflux rates, owing to cooling of the upflowing vapours before their condensation. The sugar cane spirits produced in these two types of pot still presented the lowest contents of ethyl carbamate in the present study, that is, 7.01 and 4.42 μg L^{-1}, respectively.

The lowest content of ethyl carbamate observed in the sugar cane spirit obtained using the rectifier pot still can be explained by the fact that this equipment has three interior sections made from stainless steel, which enhances the efficiency of separation, increases the reflux rate and maintains the liquid in the condenser outlet at a lower temperature, with a lower distillate flow rate.

Bruno *et al.* *(14)* also obtained sugar cane spirits with a low content of ethyl carbamate using a low temperature, a low distillate flow rate, and a high reflux rate during distillation in pot stills. The temperature in the dephlegmator, $<80°C$, drastically reduced the content of the ethyl carbamate in the distillate. On the other hand, cachaças produced in pot stills with irregular reflux rates presented high concentrations of ethyl carbamate.

The analysis of 25 different cachaça brands produced in pot stills in the state of Paraíba, Brazil, showed that distillation systems using high temperatures resulted in beverages with a higher content of ethyl carbamate (200–700 μg L^{-1}) *(16)*. By contrast, the presence of a dephlegmator and cooling system in the pot still enabled the production of sugar cane spirits with lower content of ethyl carbamate (55–100 μg L^{-1}).

It is possible to reduce the content of ethyl carbamate in sugar cane spirits by maximizing the reflux rates during distillation and minimizing the exposure of the beverage to the copper present in the descending parts of the equipment *(17)*. Our results indicate that the content of ethyl carbamate in sugar cane spirits depends on the pot still configuration as well as on the method

Table 1. Volumes, concentrations of ethanol, copper and ethyl carbamate, and distribution of the contaminant in the distillate fractions obtained after redistillation of commercial sugar cane spirit in different types of pot stills

Pot still type	Distillation fraction	Volume (L)	ABV	Copper (mg L^{-1})	Ethyl carbamate (μg L^{-1})
Hot head	Foreshots	0.40	74.17	1.65	11.31
	Spirit	14.60	71.17^{c}	1.00^{b}	14.10^{a}
	Feints	5.40	30.07	2.35	55.85
	Spent lees	16.60	0.19	32.00	179.14
Head cooler	Foreshots	0.40	78.58	3.59	5.70
	Spirit	13.80	72.26^{c}	3.70^{a}	8.02^{b}
	Feints	4.80	36.83	4.95	47.22
	Spent lees	18.00	1.45	13.16	194.93
Dephlegmator	Foreshots	0.40	83.63	0.60	5.29
	Spirit	14.10	76.51^{b}	0.20^{c}	7.01^{b}
	Feints	5.10	31.16	3.52	47.04
	Spent lees	17.40	0.15	41.10	188.29
Rectifier	Foreshots	0.40	84.19	0.42	1.58
	Spirit	13.50	79.88^{a}	0.16^{c}	4.42^{c}
	Feints	4.50	27.56	1.78	40.10
	Spent lees	18.60	0.09	29.90	198.51^{a}

Different letters in the columns indicate significant statistical difference for double distilled sugar cane spirits (Tukey test, $p < 0.05$).

of distillation. The formation of ethyl carbamate in the beverage is favoured by the high temperatures used in the process when the distillation system is defective, or presents an inappropriate configuration, or has low reflux rates.

Double distillation resulted in a significant reduction in the content of ethyl carbamate in the sugar cane spirit. After the second distillation in the different pot stills tested, 94.0–98.5% of the total ethyl carbamate formed was eliminated from the beverage. Pot stills with high reflux rates (equipped with dephlegmator or rectifying system) were more effective in reducing ethyl carbamate content in double-distilled sugar cane spirit.

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